[Second Edition.]

PATENT SPECIFICATION

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506,291

PROVISIONAL SPECIFICATION.

Improvements in the Preparation of Ion-Exchange and Acid-Removing Materials.

We, THE PERMUTIT COMPANY LIMITED, a British Company, of "Permutit House", Gunnersbury Avenue, London, W.4, and ERIC LEIGHTON HOLMES, LUCIE EVELYN HOLMES and WILLIAM GEORGE PRESCOTT, all British Subjects and all of the Company's address, do hereby declare the nature of this invention to be as follows:—

It is known that synthetic resins prepared by condensing aromatic amines or their derivatives, such as *m*-phenylene diamine, with an aldehyde or substance yielding an aldehyde on hydrolysis possess the property of removing acids from solution and can be regenerated by alkali when their capacity for removing acids or exchanging anions is exhausted. It has been found that such resins suffer from certain disadvantages in practice. For instance, the amount of water required to remove the excess alkali after regeneration is excessive, and it is almost impossible to remove the last traces of chloride when the resins are used to remove hydrochloric acid from solution.

According to the present invention, we prepare the resins as thin layers on carrier bodies, and we have found that then less wash water is required to remove the excess alkali and also that the amount of residual chlorine ions left in the effluent during a run is of much smaller amount. We believe that this improvement arises from the resin being in a thin layer instead of in the form of particles of appreciable grain size such as are used industrially. Another disadvantage the original materials possess is that if they are allowed to stand for some time in the middle of a run and the run is then completed the first portion of the effluent contains an increased amount of alkali and chlorine ions and this effluent must be run off to drain until it has been eliminated. We have also found the preparation on a carrier body results in a material which possesses these defects in only a minor degree.

Any carrier body may be used, but it is preferred to use those with some more or less porous structure, such as ground coke, charcoal, activated carbon and the like.

In preparing the resins the carrier bodies may be impregnated with one reagent so that a film is formed and then they may be treated with a second reagent. It is preferred to impregnate the carrier bodies with the amine or its derivative, dry the bodies to form a dried film and then treat them with an aldehyde in liquid or gaseous form. It is desirable that a trace of moisture should be present if the condensation is to proceed readily. The impregnation preferably takes place under vacuum, and the drying need only proceed to such an extent that the final condensation product does not glue the bodies together.

As an example of one method of preparation 100 gr. of pumice stone ground to a mesh size passing through a 20 mesh per inch screen and retained on a 30 mesh, is treated with a hot solution of 20 gr. *m*-phenylene diamine hydrochloride in 10 cc. of water, the treatment being carried out in vacuum, as impregnation of the carrier body is improved and the film of the basic hydrochloride cannot react with oxygen. The material is dried and then thoroughly mixed with 13 gr. of paraformaldehyde and heated to cause reaction to take place. This heating can be conveniently carried out in an autoclave under a steam pressure of about 10—20 lbs., but this is not essential. About 30 minutes is sufficient to complete the reaction and the resulting material is washed free from coloured impurities and is ready for use after being treated with an alkaline solution. The use of aqueous solutions of formaldehyde is not so satisfactory as they tend to dissolve out some of the basic hydrochloride before reaction is complete and the whole mass sets hard.

The formaldehyde may also be used in gaseous form, and the gas may be passed through a stirred mass of impregnated carrier or caused to flow in countercurrent to such a mass. The reaction with a gas may take place either at the ordinary temperature or at elevated

temperatures. The reaction takes much longer, of course, at the ordinary temperature.

Dated this 31st day of December, 1937.
For the Applicants:
GILL, JENNINGS & EVERY-CLAYTON,
Chartered Patent Agents,
51/52, Chancery Lane, London, W.C.2.

COMPLETE SPECIFICATION.

Improvements in the Preparation of Ion-Exchange and Acid-Removing Materials.

We, THE PERMUTIT COMPANY LIMITED, a British Company, of "Permutit House", Gunnersbury Avenue, London, W.4, and ERIC LEIGHTON HOLMES, LUCIE EVELYN HOLMES and WILLIAM GEORGE PRESCOTT, all British Subjects and all of the Company's address, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that synthetic resins prepared by condensing an aromatic amine or derivative (wholly or partly in the form of a salt), such as *m*-phenylene diamine, with an aldehyde or substance yielding an aldehyde on hydrolysis possess the property of exchanging anions in or removing acids from solution and can be regenerated by alkali when their capacity for removing acids or exchanging anions is exhausted. It has been found that such resins suffer from certain disadvantages in practice. For instance, the amount of water required to remove the excess alkali after regeneration is excessive and it is almost impossible to remove the last traces of chloride when the resins are used to remove hydrochloric acid from solution.

According to the present invention, we prepare resins having the properties referred to as thin layers on carrier bodies, and we have found that then less wash water is required to remove the excess alkali and also that the amount of residual chlorine ions left in the effluent during a run is of much smaller amount. We believe that this improvement arises from the resin being in a thin layer instead of in the form of particles of appreciable grain size such as are used industrially. Another disadvantage the original materials possess is that if they are allowed to stand for some time in the middle of a run and the run is then completed the first portion of the effluent then contains an increased amount both of alkali and chlorine ions and this effluent must be run off to drain until it has reached the desired quality. We have found that the preparation on a carrier body results in a material which also possesses these defects in only a minor degree.

Any carrier body may be used, but it is preferred to use those with some more or less porous structure; examples of suitable porous bodies are ground coke, charcoal, activated carbon and the like.

In preparing the resins porous carrier bodies may be impregnated with one reagent so that a film is formed and then they may be treated with a second reagent. It is preferred to impregnate the carrier bodies with the amine or its derivative, dry the bodies to form a film and then treat them with an aldehyde. It is desirable that a trace of moisture should be present if the condensation is to proceed readily. The impregnation preferably takes place under vacuum, and the drying need only proceed to such an extent that the final condensation product does not glue the bodies together.

As one example of a method of preparation, 100 grams of pumice stone ground to a mesh size passing through a 20 mesh per inch screen and retained on a 30 mesh is treated with a hot solution of 20 grams *m*-phenylene diamine hydrochloride in 10 cc. of water, the treatment being carried out in vacuum; as impregnation of the carrier body is improved and the film of the hydrochloride of the base cannot react with oxygen. The material is dried and then thoroughly mixed with 13 grams of paraformaldehyde and heated to cause reaction to take place. This heating can be conveniently carried out in an autoclave under a steam pressure of about 10—20 lbs. but this is not essential. About 30 minutes is sufficient to complete the reaction and the resulting material is washed free from coloured impurities and is ready for use after being treated with an alkaline solution. The average thickness of the layers of resin produced in this way is probably less than 0.5 mm.

As another example, 2.1 kilograms of *m*-phenylene diamine hydrochloride are dissolved in 900 ccs. of boiling water and stirred into 7 kilograms of ground coke to a mesh size passing through a 20 mesh per inch screen and retained on a

30 mesh. When this has been dried it is intimately mixed with 1.2 kilograms of paraformaldehyde and heated at about 100° C. until reaction is complete. If the materials are well mixed and allowed to stand, particularly in bulk, the reaction will proceed spontaneously with evolution of heat.

The use of aqueous solutions of formaldehyde is not satisfactory as they tend to dissolve out some of the hydrochloride of the base before reaction is complete and the whole mass sets hard.

The formaldehyde may also be used in gaseous form. and the gas may be passed through a stirred mass of impregnated carrier or caused to flow in countercurrent to such a mass. The reaction with a gas may take place either with or without the application of extraneous heat.

The invention includes the use of the carrier bodies with their resin films in the treatment of solutions. such as are formed when a water containing mineral salts is passed through a cation exchange material. for the exchange of anions or removal of acids from the solutions.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed. we declare that what we claim is:—

1. The preparation of synthetic resins capable of exchanging anions in or removing acids from solutions as thin layers on carrier bodies.

2. The preparation of synthetic resins capable of exchanging anions in or removing acids from solutions as thin layers on porous carrier bodies.

3. The method of forming on carrier bodies thin layers of synthetic resins capable of exchanging anions in or removing acids from solutions, which comprises forming films of one reagent on the carrier bodies and treating the bodies with a second reagent to bring about a condensation reaction on the carrier bodies.

4. A method according to claim 3, in which porous carrier bodies are impregnated with an amine or its derivative (partly or completely in the form of a salt). and the bodies are dried to form films on them and then are treated with an aldehyde.

5. A method according to claim 4. in which *m*-phenylene diamine hydrochloride is used to form the films. and paraformaldehyde is used to treat the films.

6. A method according to claim 4 or claim 5. in which there is a trace of moisture present during the condensation reaction.

7. A method according to any of claims 3 to 6. in which the films are formed under vacuum.

8. A method according to claim 3. substantially as described with reference to either of the examples.

9. The treatment of solutions by means of synthetic resins capable of exchanging anions in or removing acids from the solutions, in which the synthetic resins are employed in the form of thin layers on carrier bodies.

Dated this 8th day of December, 1938.

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